Materials and processes for microstructure fabrication

by Michael Hatzakis

The fabrication of structures considerably smaller than the devices and circuits that are mass-produced for use in computers and other electronic equipment is the subject of this paper. Devices of <1 μm (microstructures) and <100 nm (nanostructures) minimum dimensions were made possible in a practical sense only after the introduction of electron beams and the associated processes, as lithographic tools in the early 1960s. This paper presents a historical perspective of this very important chapter in lithographic technology, primarily from the point of view of materials and processes, since electron-beam systems are covered in other papers in this issue. In addition, the important criteria that have to be considered in the fabrication of small structures, with respect to the interaction of the writing beam with the resist material and the substrate, and the subsequent pattern-transferring processes, are discussed.

1. Introduction

The term "microstructure" has been used to denote physical devices with minimum dimensions much smaller than those of current state-of-the-art devices such as the bipolar or field-effect transistors (FET) used in logic or memory circuits. In the 1960s, the minimum dimensions of state-of-the-art devices were typically 5 μm; anything below 1 μm was considered a "microstructure." Today, the minimum size of production devices is down to 1 μm or less, and consequently the term "microstructures" implies devices with dimensions of 100 nm (0.1 μm) or less. In fact, a more recent term, "nanostructure," has been coined to reflect the change to nanometers (10 nm = 100 Å). Such devices are today fabricated in many laboratories for the purpose of exploring the effects of downscaling existing production devices such as FETs in silicon or III-V compounds (GaAs, for example), or for the exploration of new principles such as ballistic and quantum effects in semiconductors or tunneling effects in superconductors, magnetometers (SQUIDS), etc. In addition, new phenomena are being explored in an attempt to build switching devices with dimensions down to the molecular level (molecular electronics).

The fabrication of microstructures or nanostructures requires at least three main ingredients. First, a tool must be available that is capable of providing a writing beam smaller in diameter than the minimum structure dimensions desired. Early attempts included the use of mechanical scratching of metal layers using fine metallic probes, deep ultraviolet contact-printing techniques, ion probes, X-ray printing, etc. The most prominent tool, however, has been and continues to be electron beams. This is not unexpected, considering that electron microscopy has demonstrated resolution superior to that of any other technique, at least up to the most recent development of the scanning tunneling microscope (STM). In the 1960s, A. V. Crewe at the Argonne National Laboratory demonstrated that a spatial resolution of 30 Å could be obtained with scanning

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transmission microscopy [1]. This claim re-established the belief that fine electron probes can be formed with diameters much smaller than those of any device being considered today.

The second ingredient in microstructure fabrication is the recording medium onto which the desired device pattern is written by the beam. This medium, often referred to as "resist," must be sensitive to the writing beam (electron, X-ray, UV, etc.), or it must be altered by the beam in such a way that, after development, the portion exposed to the beam is removed (positive resist) or remains on the workpiece after the unexposed portion is removed (negative resist). Resist materials are, in general, polymeric solutions that are applied onto the surface of the workpiece by spinning techniques and are dried to form a thin uniform layer of thickness depending on the application and the resolution (minimum linewidth) required.

The third ingredient is the process of transferring the pattern developed in the resist onto the actual surface of the workpiece in order to form the desired device structure. In this respect, the resist is only a temporary layer that is, in most cases, removed after the transferring process has been completed. During this process, the resist is used as a "mask" through which materials, such as metals for the formation of conductors (metallization) or impurities (ion implantation), can be added to the surface of the workpiece; or it can be used as a mask for the removal of materials, such as oxides or metals, or the etching of trenches in the substrate itself.

The combination of tool, resist, and the associated processes is referred to as "lithography," a term from the Greek meaning "writing on stone," an ancient art used for engraving, painting, etc.

2. Historical perspective

Lithography in its present form has been practiced for the fabrication of solid-state devices since the 1950s, when the planar process for mass production of silicon transistors was developed at Bell Laboratories. As the name implies, the planar process starts with a flat silicon wafer with one polished surface onto which, through a series of lithographic steps, one can fabricate discrete devices or complete integrated circuits for logic or memory applications. The number of devices or functions that can be included in a fixed surface area of the wafer or chip depends on the lithographic process resolution, or the minimum linewidth that can be transferred onto the surface of the wafer and the accuracy with which this linewidth can be maintained within one chip or between chips.

By the early 1960s, lithography had progressed to the point where integrated circuits with minimum device linewidth of 5 μm were mass-produced, using primarily optical-lithography tools operating at a wavelength of approximately 400 nm and using photographic emulsion masks with a contact-printing technique to expose the pattern onto the photoresist-coated silicon wafer.

One of the major limitations to pattern resolution in the 1960s was the photoresists; these were derived from materials used in the printing industry, mainly supplied by Kodak, and consisted of cyclized rubbers (polyisoprenes) sensitized to UV light with bis-azides or polyvinyl-cinamates with similar sensitizers [2]. These rubbery materials exhibit some swelling during development, due to solvent absorption, thereby limiting the minimum line or space that could be reliably obtained to 2–4 μm, depending on resist thickness.

The most important development in photoresists was the introduction, in the mid-1960s, of the AZ series of resists by the Shipley Company through a licensing agreement with Azoplate, a subsidiary of the Hoechst Corporation. These resists are positive in tone and contain a phenol formaldehyde resin and a benzoquinone diazide as sensitizer. AZ resists are optimized for exposure at a wavelength of 400 nm and are developed in a basic water solution with practically no swelling; therefore, very high resolution is possible. Many other positive photoresist systems with similar compositions and properties have been produced by various chemical companies since then. The most important contributions of the AZ-type photoresist were 1) that lithographic resolution was no longer limited by the resist, but rather by the exposing optical tools and the processes, and 2) that the pattern linewidth could be adjusted (biased) by longer or shorter photoresist development time. This realization placed the burden of improving image resolution upon the lithographic tool manufacturers. In addition, at this time resolution of optical (UV) lithographic tools was assumed to be limited to no better than 2-μm minimum linewidths due to diffraction and other lens aberrations. Hence, it was felt that other forms of radiation should be investigated. At this time, electron-beam probes of a diameter smaller than 10 nm (100 Å) could be rather easily obtained, as demonstrated by the emerging scanning electron microscope (SEM), developed at Cambridge University, England. Experiments were initiated and special groups were set up in various research laboratories such as IBM Research (Yorktown), Westinghouse Research, Texas Instruments, Hughes Research, and Philips Research (England), to investigate the possibilities of using electron beams in device fabrication and to explore ways of controlling the beam for writing the circuit pattern. The first attempts in IBM included the use of an optical system which scanned a large transparency (8 × 10 inches) and derived a beam-blanking signal which controlled the "on" and "off" conditions of the beam that synchronously scanned a much smaller (1-mm^2) field size on the workpiece placed under the electron beam. Light was provided by a 2 × 3-inch high-resolution CRT (cathode ray tube) that was magnified by a large lens to cover the 8 × 10-inch transparency. A schematic of the system is shown in **Figure 1**. With this system, and others

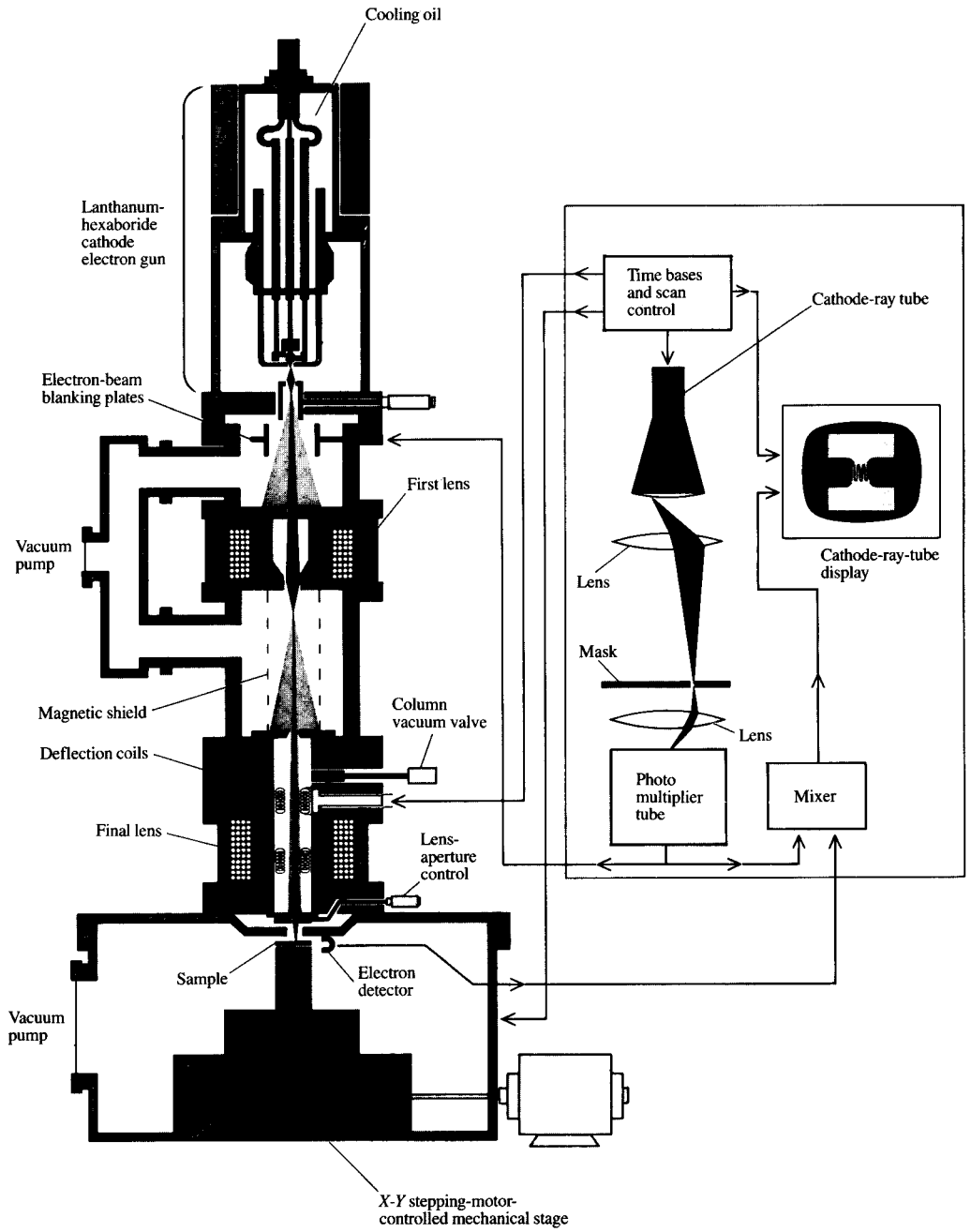


Figure 1

Optical-scanner-controlled electron-beam exposure system.

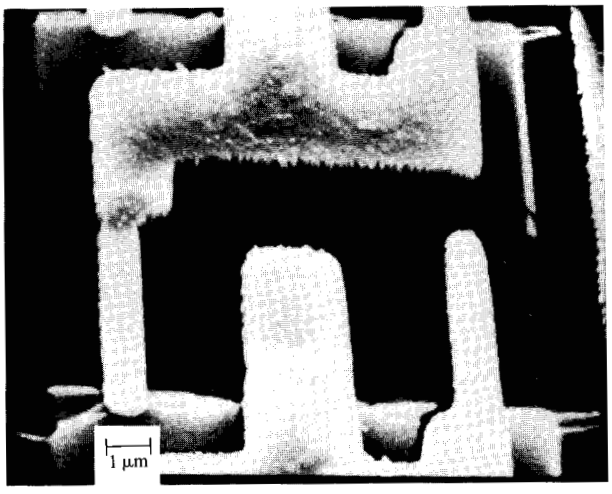


Figure 2

Scanning electron micrograph of one stage of an eleven-stage ring oscillator fabricated at IBM using PMMA, ion implantation, and the lift-off process with 1-μm-gate-length FETs. The optical-scanner-controlled electron-beam system shown in Figure 1 was used for all the exposure steps.

built at several research laboratories, a predetermined pattern could be written on the workpiece by an electron beam of diameter much smaller (10–50 nm) than that of any circuit or device contemplated at this time. Before this could occur, however, a recording medium had to be found that would respond to electron-beam radiation and be capable of resolving patterns with such dimensions. All of the existing photoresists, and many other materials, were tested for this purpose in all laboratories capable of writing patterns with electron beams. In this respect, the most important discovery in the mid-1960s was that polymethyl methacrylate (PMMA) was sensitive to electron-beam radiation as a positive-tone resist with very high resolution capabilities [3].

Shortly afterward, a metallization process was discovered that made it possible to transfer the pattern developed in the resist into a metal or other conductor pattern with no loss in resolution. This was very significant at a time when all metallic conductor patterns, required for the electrical connections of devices and circuits, were defined by wet chemical etching of metal films using resists as masks. That process was limited in resolution to about 2-μm linewidth, due to undercutting effects in the metal-etching process. The new additive metal process made use of the naturally undercut profile obtained after development of an electron-beam-exposed resist such as PMMA, and became known as the "lift-off" process [4]. With the lift-off process, it was shown that the resulting metal width was an exact duplicate of the developed line in the resist, at the resist surface; therefore, any resolution improvement obtained by the use of electron beams and PMMA resist could easily be realized in the metal pattern as well [5].

With PMMA electron resist, the new metallization process, and experimental electron-beam writing tools, the way was now open for the fabrication of very small devices in many research laboratories—Texas Instruments, Westinghouse, Bell Labs, Philips Research, Hughes, and IBM. The first devices fabricated included scaled-down silicon bipolar transistors and field-effect transistors (FET) with minimum emitter and gate lengths of 1 μm or less [6–9]. **Figure 2** is a scanning electron micrograph of the first eleven-stage ring oscillator with enhancement-depletion-mode FETs of 1-μm gate length fabricated with PMMA, ion implantation, and the lift-off process (see [7]).

Other types of devices fabricated at this time include interdigital acoustic surface wave transducers for delay-line applications. For microwave applications, the center-to-center line spacing of those transducers should be of the order of 0.2–0.5 μm. Such devices were fabricated using PMMA and aluminum lift-off on lithium niobate crystals with minimum linewidth ≃ 100 nm [10]. Also, the old idea of using Fresnel zone plates as X-ray imaging elements (lenses) was tried, with the goal of building an X-ray microscope with resolution higher than that obtained from the best optical microscopes. For a resolution better than 100 nm, the outer zones of the zone plate should be narrower than 100 nm. **Figure 3** shows the two views of an experimental free-standing zone plate fabricated with electron-beam exposure of PMMA resist and gold lift-off. The narrowest outer zone is 70 nm (700 Å).

The ability to fabricate very small structures has also stimulated research into other physical phenonema such as one-dimensional superconductors [11], magnetoresistive devices [12], superconductive quantum interference devices (SQUIDs) [13], and, recently, quantum wells (*IBM Journal of Research and Development*, Vol. 32, No. 3, May 1988).

By the mid-1970s, electron-beam exposure systems with pattern generators entirely under computer control had been developed in many laboratories. With these systems, a hard-copy mask was no longer required, since the pattern information was stored in magnetic tapes or disks and transferred directly to the pattern generator and to the other functions of the systems such as mechanical stage movement, beam on and off, etc. [14–16].

Specialized electron-beam systems are used today to fabricate optical masks for production UV tools [17], integrated circuits such as personalization of gate arrays directly on silicon wafers [18], or nanostructures down to 100 nm and smaller [19].

3. Resists and processes for structure fabrication

As mentioned in the Introduction, a high-resolution writing tool is not by itself sufficient for fabricating very small

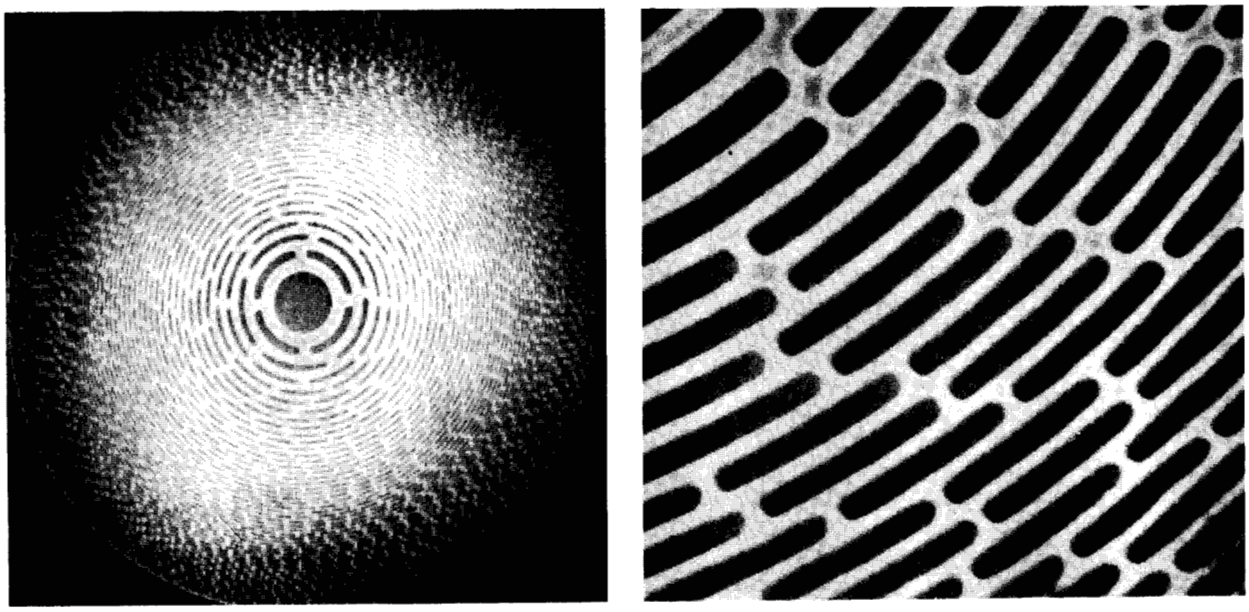


Figure 3

Zone plate fabricated with electron-beam exposure of PMMA resist and gold lift-off (free-standing). A view of the whole zone plate is shown at left (diameter 20 μm) and a magnified view at right. Minimum zone width is 70 nm.

structures; a medium must also be found that is able to record and reproduce the features of the structure on the substrate or workpiece without loss in resolution. The reproduction of the structure is, in general, a two-step process; first, the structure is "developed" in the recording medium or resist, and subsequently it is transferred to the substrate by either an additive or a subtractive process. Although all semiconductor devices, integrated circuits in production with optical UV tools, etc., are manufactured today according to the same principles [20], nanostructure fabrication requires the use of special resists and processes because minute pattern distortions in the resist or the transfer process can be catastrophic for such small structures.

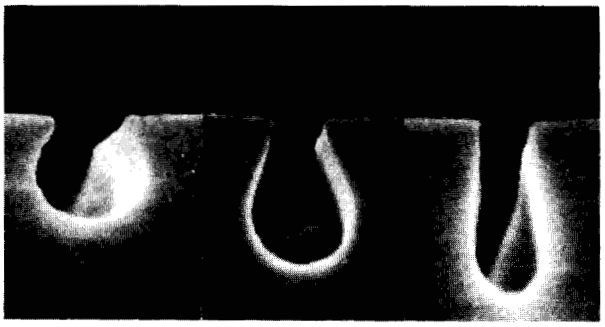
In many respects, the resist and the transfer process are interdependent; for example, the choice of resist system depends on the process constraints, and conversely, certain resists are not very useful for some transfer processes. For this reason, it is very difficult to separate resist and process in a discussion of small-structure fabrication. The approach taken in this paper is to discuss the pattern transfer processes, namely additive and subtractive, and to attempt to describe resists and processes most suitable for each.

- *Additive processes*

Lift-off processes

As mentioned in the previous section, polymethyl methacrylate (PMMA) resist was found to be most suitable for microstructure fabrication (see [10]). This fact was later demonstrated more convincingly by Broers [21] when he fabricated structures in PMMA as small as 20 nm. Also, as shown earlier (see [5]), electron-beam exposure of a positive resist, such as PMMA, results in an energy absorption profile that is pear-shaped, or wider at the bottom than at the top of the resist [22]. This energy absorption profile results in a similar resist profile after development, which has been called "undercut," or "re-entrant." Undercut profiles were first observed in PMMA resist [23] and were used extensively to study the energy dissipation of electron beams in solids [24], as shown in **Figure 4**. These resist profiles inspired the first experiments on metallization based on evaporation of the metal using the undercut resist as "stencil." Since the resist remains soluble, soaking the structure in a good resist solvent lifts the unwanted metal over the resist while the desired metal structure remains on the workpiece, hence the name "lift-off" (see [4]).

The lift-off process has been used extensively for the fabrication of the first experimental devices and is also used today both for experimental work in nanostructure fabrication and in the production of both logic and memory VLSI circuits by some manufacturers of ICs [25–27]. Some of the attributes of the lift-off metallization process are that it is simple, it does not require sophisticated and expensive equipment, and it can be used to pattern any material, metal or insulator, that can be deposited by evaporation, including multilayer structures of various compositions. For the



(a) (b) (c)

Figure 4

Electron energy dissipation profiles at various electron accelerating potentials: (a) 10 kV, (b) 15 kV, (c) 25 kV. The recording medium is a PMMA film of thickness greater than the maximum electron penetration range at 25 kV.

successful application of the lift-off process in any situation, however, certain requirements must be met, some of which are related to the resist and others to the exposing and evaporation tools:

a. The resist profile angle to the surface normal must always be larger than the evaporation angle. This is illustrated in **Figure 5**, where the resist angle α should be larger than the evaporation source angle β to ensure that metal is not deposited on the undercut resist wall, so that a discontinuity between the metal deposited on the resist surface and the metal on the substrate is maintained. Without this discontinuity, it would be impossible to separate the two metal layers during lift-off. For the same reason, the resist layer thickness should always be greater than the metal thickness, as is also indicated in Figure 5, in order to allow solvent to penetrate and dissolve the resist under the metal.
b. The temperature stability of the resist stencil, which is determined by the softening point of the polymer [or the glass transition temperature (T_g)], above which the resist will flow and cause distortion of the developed image, including loss of the undercut profile, should not be exceeded during metal evaporation or cleaning. For example, PMMA resist flows above 110°C to the point where lift-off cannot be accomplished; therefore, care should be taken not to exceed 100°C temperature on the substrate during evaporation.
c. Care also should be taken after resist development to clean the substrate surface thoroughly in the open areas by means of a long rinse cycle with a nonsolvent for the resist, or by chemical or plasma etching methods, so that good adhesion and low contact resistance of the metal with the substrate is maintained.
d. The resist should remain soluble in some solvent or liquid after metal evaporation; otherwise, lift-off cannot be completed. In some cases, ultrasonic agitation may be necessary in order to lift off the unwanted metal, although this should be used only as a last resort, since the metal pattern on the substrate may also be damaged.

As mentioned earlier, the idea for the lift-off process was conceived after it was observed that electron-beam-exposed PMMA resist exhibits undercut profiles after development. It was also shown subsequently that the amount of undercut depends on the material and on the exposure dose. In general, for PMMA and a developer consisting of a mixture of isopropanol and methyl-isobutyl-ketone, an electron-

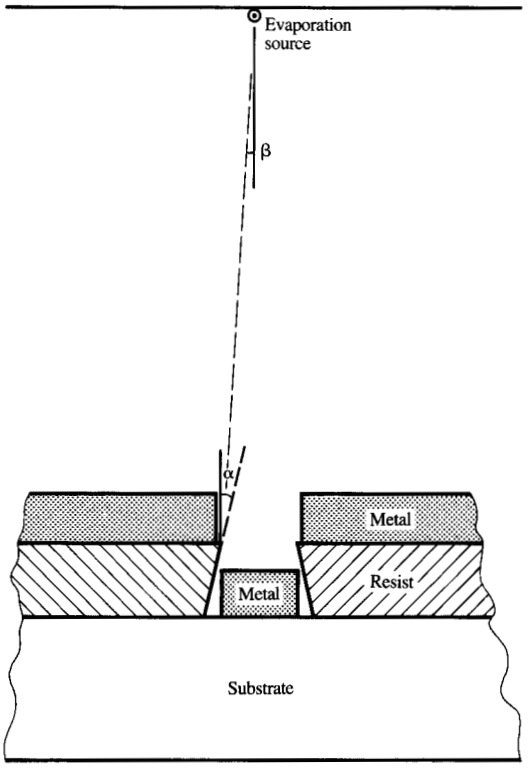


Figure 5

Lift-off process requirement indicating that the resist undercut angle α should be greater than the evaporation angle β, and that resist thickness should be greater than metal thickness in order to maintain discontinuity between the metal on the substrate and the metal over the resist.

beam dose of at least 100 $\mu C/cm^2$ at 20 kV is required to obtain undercut profiles suitable for lift-off [28]. The undercut angle can be increased only slightly by a further increase in exposure dose before significant line widening is observed. If larger undercut angles are desired with PMMA resist, the only possibility is to decrease the electron-beam accelerating voltage to 10 kV or less if the exposure system design allows.

In order to increase resist sensitivity and temperature stability, copolymers of polymethyl methacrylate and methacrylic acid have been developed that exhibit a fourfold increase in sensitivity over PMMA and a resist profile stability at temperatures of at least 150°C [29]. Unfortunately, with these resists it is difficult to obtain undercut profiles suitable for lift-off. Significant improvements in both undercut angle control and resist sensitivity have been obtained with multilayer resist structures.

Although many multilayer resist systems have been developed today for a variety of applications [30, 31], the discussion here is limited to systems intended for electron-beam lithography.

As was shown in [22], the solubility of PMMA resist in a given solvent, such as methyl-isobutyl-ketone (MIBK), depends on the molecular weight of the polymer. If two lots of PMMA resist, one of low and one of high molecular weight, are spin-coated on the substrate in succession, with a baking step at 160°C after each spinning, two separate resist layers can be formed. After electron-beam exposure of the two-layer film and during development, the top layer develops slowly due to its higher molecular weight, even in the exposed areas; when the bottom layer is reached, development proceeds faster, resulting in undercut-like profiles [32]. The undercut angle can be adjusted independently of exposure dose, by overdevelopment or underdevelopment. In general, developers for this two-layer PMMA resist scheme are mixtures of methyl-isobutyl-ketone (MIBK) and isopropanol (IPA) in various proportions. In fact, the choice of developer is rather difficult because, for a given exposure dose, a developer must be selected that develops the top layer at a practical rate (not too slowly), yet develops the bottom layer slowly enough that the amount of undercut can be easily controlled.

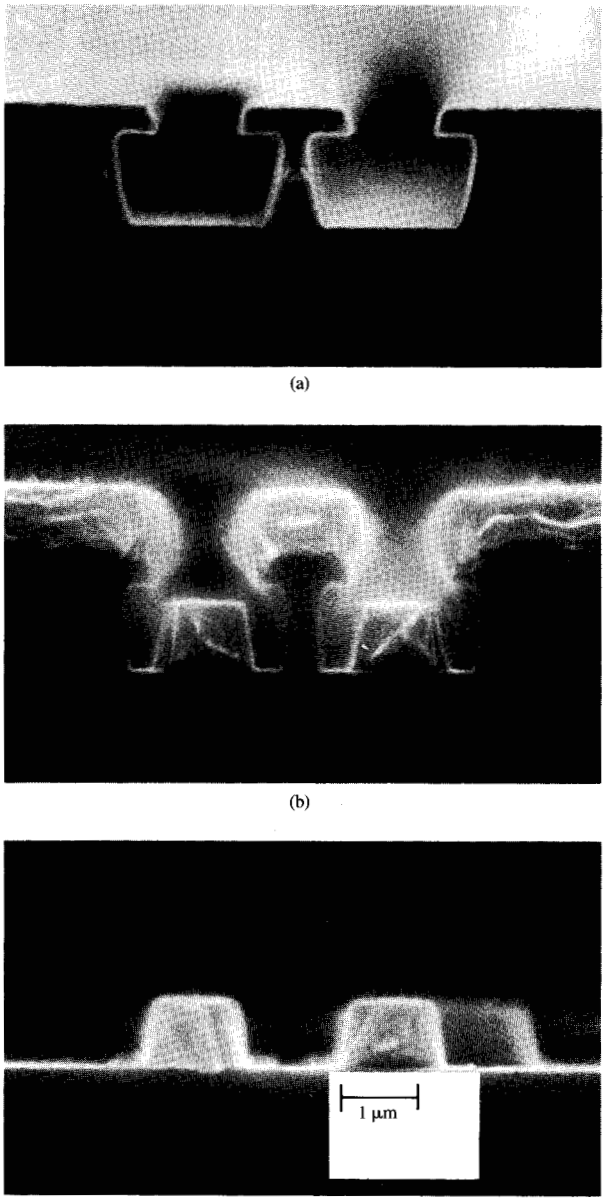
A more practical combination of a two-layer resist has been reported and is widely used for nanostructure fabrication in which the two resist layers require completely different and mutually exclusive developers. With this combination, the top resist layer is developed first to the desired linewidth, then the developer is changed and the bottom layer is developed to the desired undercut profile, with no further change in the top layer pattern. The two resist layers that can be used in this manner are PMMA and the copolymer of methyl methacrylate and methacrylic acid [33]. As **Table 1** shows, PMMA is soluble in nonpolar solvents in which the copolymer is completely insoluble; similarly, the copolymer is soluble in polar solvents, like alcohol, where PMMA is completely insoluble. This resist system has been used extensively with the copolymer as the top layer [34] to fabricate 1-μm memory arrays with the lift-off technique at electron-beam exposures of 10–20 $\mu C/cm^2$, at which dose no undercut profile can be obtained with either PMMA or copolymer alone [35]. Typical profiles obtained with this resist system are shown in **Figure 6** (a) before metal evaporation, (b) after evaporation of one micrometer of aluminum, and (c) after lift-off.

Table 1 Solubility of P(MMA-co-MAA) and PMMA at 10^{-5} C/cm^2 electron-beam exposure.

	Polar solvents (alcohols, ethers)	*Nonpolar solvents (aromatic solvents)*
PMMA	Low (100 Å/min)	Very high (10K Å/min)
P(MMA-co-MAA)	High (2K Å/min)	Zero

Since the resists are developed in mutually exclusive developers, it is also possible to reverse the position of the two layers by spinning the copolymer first, with the PMMA on top. This combination has been already reported for the fabrication of 40-nm-wide lines [36] using aluminum lift-off. The requirements for any two-layer resist system in which both layers are sensitive resists of the positive tone, or resists that degrade on irradiation and become more soluble in a given solvent, are intimately related to the resist-solubility-rate ratio between exposed and unexposed areas at a particular exposure dose. These requirements can be summarized as follows:

a. *Top layer* The solubility-rate ratio in the top resist developer should be high enough to ensure that the resist layer after development is thick enough to be able to withstand the metal evaporation over it without collapsing, since this layer will form the overhang after development.
b. *Bottom layer* Ideally, the sidewall of the bottom layer after development should be vertical or as steep as possible, to ensure maximum resolution and to prevent metal accumulation at the resist edge that creates "fences" at the edges of metal lines due to shallow resist profiles. An example is given in **Figure 7**, where the top diagram shows three different cases. In the first case, PMMA is used as the bottom layer and the stack is exposed at 10 $\mu C/cm^2 (Q = 10^{-5}\ C/cm^2)$, with a solubility-rate ratio in chlorobenzene of 1:3. The dotted line labeled 1 will be the resultant bottom-layer profile and, as it is easy to see, the 1-μm space will be completely undercut



(a)

(b)

(c)

Figure 6

SEM photos of the double resist layer process with 1.4-μm-thick PMMA as the bottom layer and 0.4-μm-thick copolymer as the top layer, exposed at 20 μC/cm^2: (a) resist profile after development in ethoxyethanol-isopropanol mixture for the top layer and chlorobenzene for the bottom layer; (b) same structure after a 1-μm-thick aluminum evaporation; (c) aluminum lines after lift-off.

and lost. In the second case, the same stack is exposed at 25 μC/cm^2, where $R/R_0 = 2.8$, and profile 2 will be obtained after development. Again, the 1-μm space will be almost completely undercut. This case has been verified experimentally and is shown below in the SEM at left (2). In the third case, the copolymer is placed at the bottom of the stack and the PMMA on top. At an exposure dose of 10 μC/cm^2, the solubility-rate ratio of copolymer in a 1:1 mixture of ethoxyethanol-IPA, $R/R_0 = 13$; under this assumption, profile 3 results. This case is also confirmed by experiment, as shown in the SEM labeled 3 at the bottom right of the figure.

These results demonstrate that a solubility-rate ratio of at least ten ($R/R_0 = 10$) is required for the bottom resist layer to obtain reasonably vertical profiles. The amount of undercut (or overhang in the top layer) can be controlled by over- or underdevelopment of the bottom layer. Again, the thermal stability of both resist layers must be higher than any temperature to which the sample may be subjected during processing.

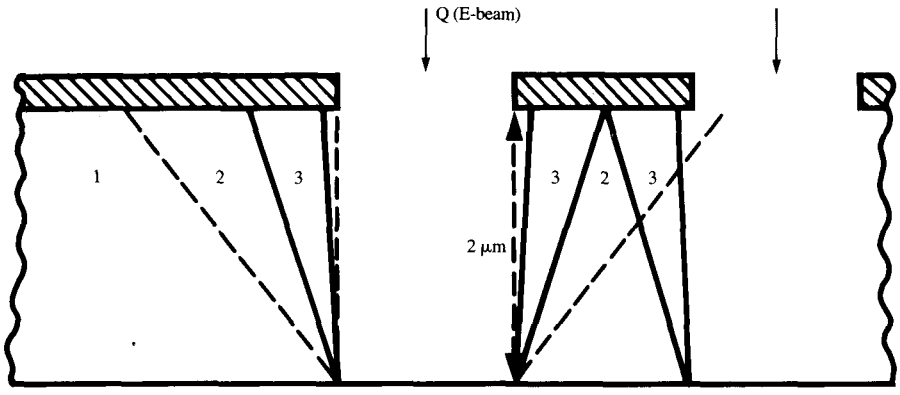
The three resist systems discussed so far [single-layer PMMA, two-layer PMMA, and two-layer PMMA-P(MMA-co-MAA)] represent the most commonly used processes for lift-off in nanostructure fabrication. For larger dimensions and production-oriented processes for integrated circuit fabrication (memory and logic), various resist systems have been developed for electron-beam as well as optical lithography tools. Many of these schemes are described in [25–27].

Plating processes

The second additive metallization technique, which has found uses in circuit-board fabrication and also in microlithography, although not yet in nanolithography, is plating in areas of the pattern not covered with resist or, as in lift-off, using the resist pattern as a stencil for plating.

For microlithography, the most common technique has been electroplating, in which a conductive layer of a plating base is needed under the resist, usually gold, which must be continuous on the entire workpiece so that electrical connection can be made to it during plating. The basic process is shown in **Figure 8**. Electroplating was used extensively for the fabrication of conductor patterns in magnetic bubble memories during the 1970s [31] and is also used today for the fabrication of X-ray masks [37–39].

As mentioned above, one of the requirements of the electroplating process is that a continuous conductive layer must be placed under the resist and that the resist must adhere to it during pattern development and during plating. Marginal adhesion can cause plating under the resist and eventual resist lifting in the plating bath. Another requirement is that the exposed plating base, after resist development, must be throughly cleaned of any organic residues, or the metal will not plate uniformly. This cleaning can be accomplished by extended rinses in various solvents and deionized water followed by plasma ashing in oxygen to remove any traces of organics.



1. PMMA at $Q = 10^{-5}$ C/cm^2, $R/R_0 = 1.3$.
2. PMMA at $Q = 2.5 \times 10^{-5}$ C/cm^2, $R/R_0 = 2.8$.
3. Copolymer at $Q = 10^{-5}$ C/cm^2, $R/R_0 = 13$.

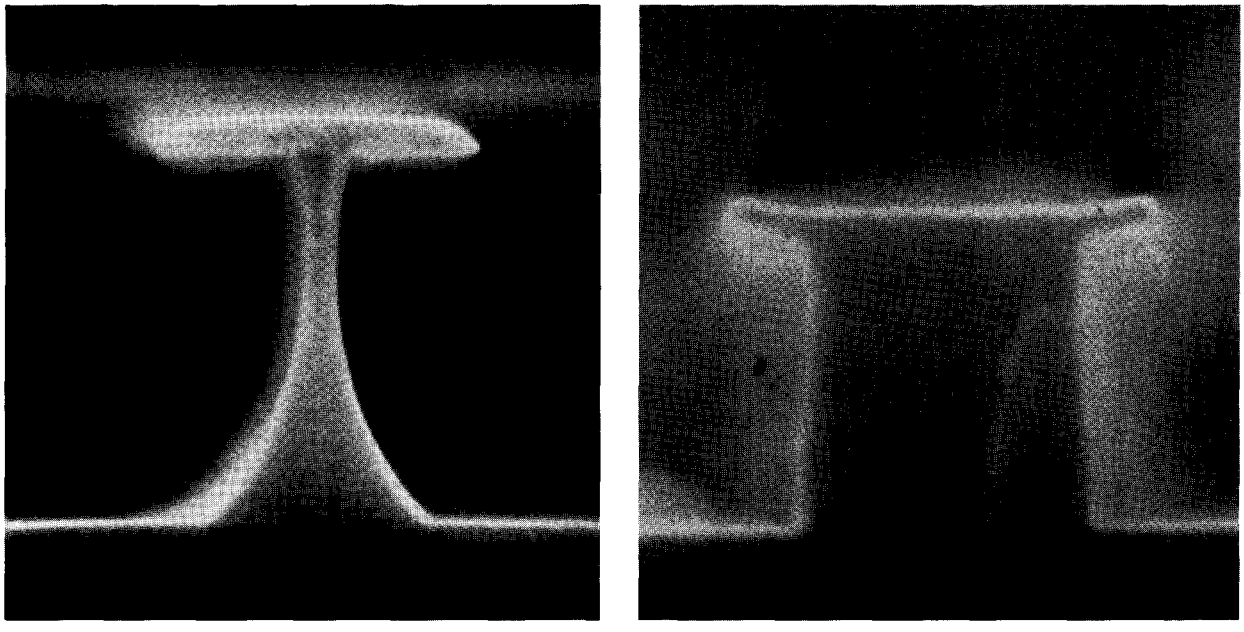


Figure 7

Illustration of the dependence of resist profile shape on the solubility rate ratio (R/R_0) of the bottom resist layer in a two-layer system using PMMA and copolymer P (MMA-co-MAA) as the two resists: (1) PMMA as the bottom layer exposed at 10 μC/cm^2. (2) Same as in 1 but exposed at 25 μC/cm^2, and SEM showing actual profile under these conditions, at bottom left. (3) Copolymer as the bottom layer, exposed at 10 μC/cm^2, and actual SEM at bottom right.

The third requirement is that the resist profile after development should be as vertical as possible, so that sharply defined rectangular metal line profiles can be obtained as required for X-ray mask absorber pattern fabrication and for producing very-high-resolution patterns. PMMA and the copolymers of methyl methacrylate and methacrylic acid can

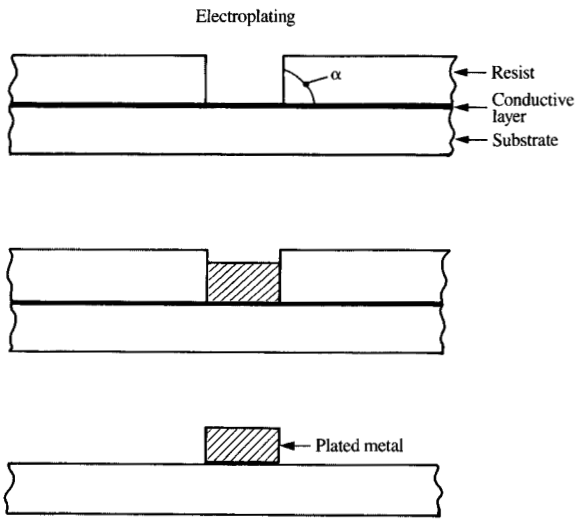


Figure 8

Schematic of the plating process through a resist mask.

be exposed and developed under conditions that produce vertical profiles, as shown in [28]; both have been used for high-resolution patterns in magnetic bubble devices and X-ray mask fabrication.

Figure 9 shows, on the left, a scanning electron micrograph of the plated pattern through copolymer resist, and, on the right, the gold pattern after removal of the resist. Also, plating through cracks in the resist (unintentional), as shown in [38], indicates that the process of electroplating with gold could be extendable to very small linewidths. This is also shown by Kern et al., who were able to fabricate 100-nm lines for zone plates by plating through PMMA (see [19]).

• *Subtractive processes*

Subtractive patterning processes comprise all processes in which the material to be patterned is applied first to the workpiece as a uniform layer, followed by the resist, which is patterned over the layer, with, finally, removal of the unwanted materials. The most common of these is the use of wet chemical etching solutions (acids or bases) to pattern metallic conductors for integrated circuit fabrication or thin chromium layers for optical mask fabrication. This process, using photoresist as the mask over the metal, has been used for many years and is still used for circuits with minimum

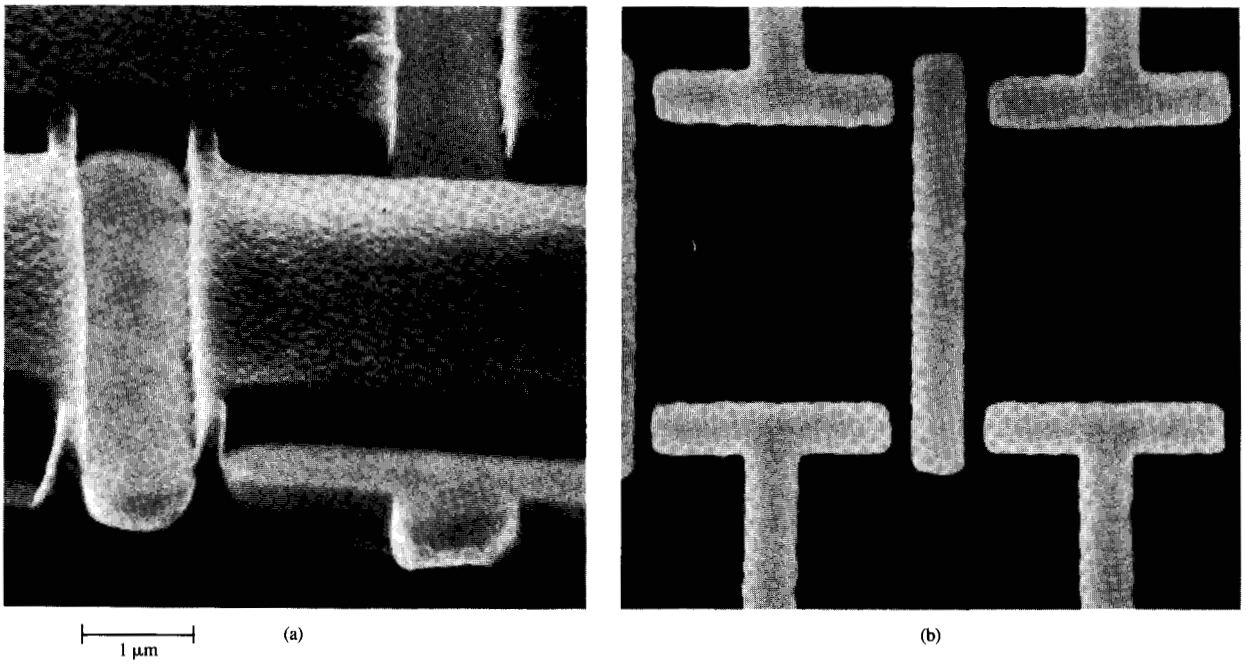


Figure 9

(a) Gold pattern electroplated through copolymer resist; (b) same after resist and planting base removal.

features of 3 to 4 μm and metal thicknesses of 1 μm or less. The resolution limitation of wet chemical etching is a direct result of undercutting or metal etching under the resist mask due to the isotropic nature (equal etching rate in the vertical and horizontal directions of a metal line) of the chemical etch. Subtractive patterning became useful for microstructure fabrication only after the development of dry-etching processes such as ion milling and reactive-ion etching (RIE), which can be highly anisotropic (etching only in a direction perpendicular to the metal or other layer surface).

Some early work on microstructure fabrication utilized electron-beam polymerization of diffusion pump oils purposely introduced in the vacuum chamber or from the residual vapors present in any system pumped by a diffusion pump. Very fine lines were written on gold in this manner, and the gold was subsequently ion-milled using this polymerized oil as a mask [40, 41]. Later, Broers and co-workers showed that lines as small as 8 nm can be fabricated in this manner [42].

This process, however, is very slow and is dependent upon the residual vapor pressure in the system. Many similar attempts have been made since, but none so far have shown promise as a practical microfabrication process. The most successful subtractive patterning process by far is reactive ion etching (RIE), both for the production of integrated circuits, in silicon, SiO_2, and metal patterning processes, and for microlithography.

Most of these processes use a resist as the mask, and in general, fluorine-containing gases for silicon and SiO_2 and chlorine for aluminum or aluminum–copper alloys, in a parallel-plate reactor with the bottom plate (where the samples are placed) powered by a 13.5-MHz RF source [43]. Since the resists used also etch away during patterning, the RIE plasma parameters, such as power, pressure, gas flow, and gas composition, have to be optimized in order to reduce the resist-to-material etch-rate ratio. In general, acrylic-type polymer resists, such as PMMA and copolymers of PMMA, are not very stable and therefore not very useful in RIE transfer processes, while phenolic-type polymers, such as the Novolac resins, are much more stable and are more widely used. Novolac-type resin is the main ingredient in most commercial photoresists and in some electron resists such as NPR, developed at Bell Laboratories [44]. However, the resolution of these resists has not been demonstrated to levels of 100 nm or less, and for this reason nanolithography has been limited to lift-off and ion milling with acrylic polymers.

Other processes that have been proposed to overcome this problem include three-layer (trilayer) resist schemes in which a Novolac-type polymer is used as the RIE mask but not as the pattern-defining resist. A thin inorganic or organometallic layer, such as SiO_2 or glass resin, is coated over the Novolac resin after curing, and a pattern-defining resist is spin-coated over the inorganic layer. After exposure and development of this top resist layer, the pattern is transferred to the inorganic layer by RIE in fluorine gas, after which oxygen RIE is used in turn to transfer the pattern to the Novolac resin using the inorganic layer as a mask [45, 46]. **Figure 10** shows a scanning electron micrograph of a pattern defined in a tri-layer resist by electron-beam exposure and transferred by RIE in the silicon substrate (J. Paraszczak, private communication, IBM Thomas J. Watson Research Center, Yorktown Heights, NY 10598).

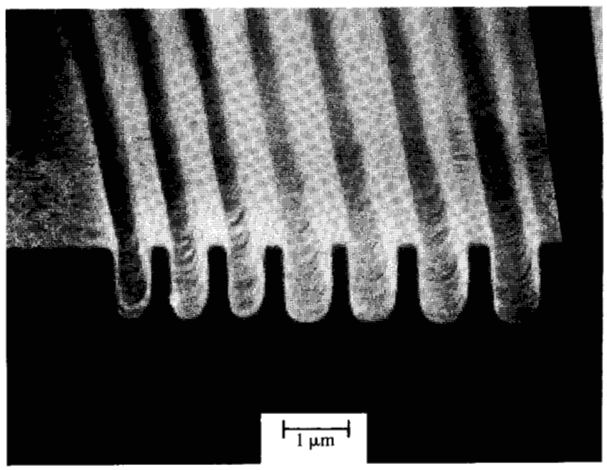


Figure 10

SEM of pattern transferred in silicon by RIE using an electron-beam-exposed tri-layer resist system. The resist has been removed.

A recent approach makes use of organometallic polymers, such as siloxanes, which are sensitive electron-beam resists, to eliminate one layer by combining the functions of resist and RIE mask into one. This process, therefore, uses the same Novolac polymer layer first, upon which, after curing at 200°C, the siloxane resist is spin-coated, exposed, and developed, and the pattern is transferred by oxygen RIE to the Novolac layer [47]. **Figure 11** shows SEM profiles of 0.25-μm lines and spaces exposed on siloxane resist and transferred by RIE to the thick Novolac layer.

Many similar materials and processes have been developed based on the same principle; however, none of these has demonstrated structures with features smaller than 100 nm.

4. Conclusion

In this paper one view of the history of microfabrication has been presented and discussed, with particular emphasis on the development of the technology that led to the fabrication of structures smaller than 100 nm (nanofabrication). Some of the more relevant materials and processes have been

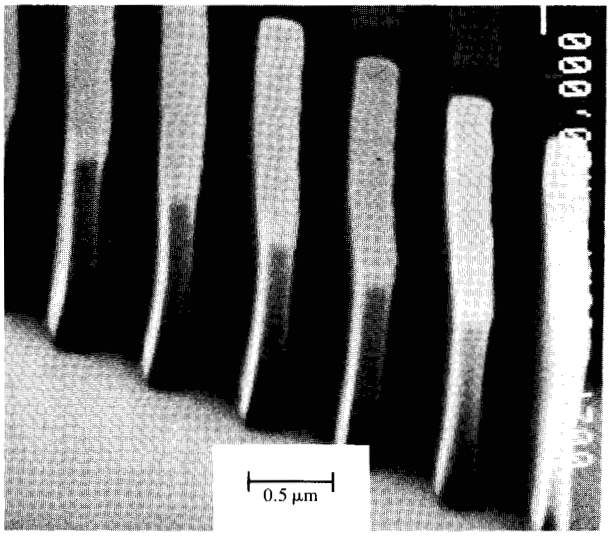


Figure 11

SEM of 0.25μm lines and spaces exposed by electron beam in siloxane resist and transferred by RIE to the bottom thick polymer layer.

outlined, emphasizing those applicable to nanolithography. Many other interesting materials and processes have been omitted in the interest of space, such as shadowing and sidewall techniques that can produce nm lines using the sidewalls of rather large patterns defined by electron-beam or even optical lithography [48]. Although very small structures can be produced with this technique, a limited number of shapes can be fabricated.

Another interesting method utilizes interference of two very-short-wavelength laser beams with a phase difference. Again, very small lines can be produced, but the technique is limited to periodic structures only (see [48]).

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